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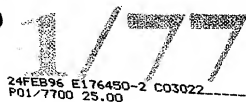
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Dated

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22 FEB 1996

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1. Your reference

8716

2. Patent application number

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9603770.0

3. Full name, address and postcode of the or of each applicant (underline all surnames)

BP CHEMICALS LIMITED
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Patents ADP number (if you know it)

4141391002

If the applicant is a corporate body, give the country/state of its incorporation

ENGLAND, UNITED KINGDOM

4. Title of the invention

ESTER SYNTHESIS

5. Name of your agent (if you have one)

"Address for service" in the United Kingdom to which all correspondence should be sent (including the postcode)

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Patents ADP number (if you know it)

5623925001

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Country

Priority application number
(if you know it)

Date of filing
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Number of earlier application

Date of filing
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8. Is a statement of inventorship and of right to grant of a patent required in support of this request? (Answer 'Yes' if:

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Patents Form 1/77

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Continuation sheets of this form

Description 16

Claim(s) -

Abstract -

Drawing(s) -

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Priority documents

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Statement of inventorship and right to grant of a patent (Patents Form 7/77)

Request for preliminary examination and search (Patents Form 9/77)

Request for substantive examination (Patents Form 10/77)

Any other documents (please specify)

11. I/We request the grant of a patent on the basis of this application.

Signature *M. Krishnan* Date

KRISHNAN, Suryanarayana Kalyana 22 February 1996

12. Name and daytime telephone number of person to contact in the United Kingdom 01932 762734

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ESTER SYNTHESIS

The present invention relates to a process for the synthesis of esters by reacting an olefin with a lower carboxylic acid in the presence of an acidic catalyst.

It is well known olefins can be reacted with lower aliphatic carboxylic acids to form the corresponding esters. One such method is described in GB-A-1259390 in which an ethylenically unsaturated compound is contacted with a liquid medium comprising a carboxylic acid, a free heteropoly acid of molybdenum or tungsten. This process is a homogeneous process in which the heteropolyacid catalyst is unsupported. A further process for producing esters is described in JP-A-05294894 in which a lower fatty acid is esterified with a lower olefin to form a lower fatty acid ester. In this document, the esterification reaction is carried out in the gaseous phase in the presence of a catalyst consisting of at least one heteropolyacid salt of a metal eg Li, Cu, Mg or K, being supported on a carrier. The heteropolyacid used is phosphotungstic acid and the carrier described is silica.

It has now been found that the process efficiency can be improved significantly by using a specific carrier.

Accordingly, the present invention is a process for the production of lower aliphatic esters said process comprising reacting a lower olefin with a saturated lower aliphatic mono-carboxylic acid in the vapour phase in the presence of a heteropolyacid catalyst on a siliceous support characterised in that the siliceous support is in the form of extrudates or pellets.

The siliceous support used is most preferably derived from an amorphous, non-porous synthetic silica especially fumed silica, such as those produced by flame hydrolysis of SiCl_4 . Specific examples of such siliceous supports include Support 350

made by pelletisation of AEROSIL® 200 (both ex Degussa). This pelletisation procedure is suitably carried out by the process described in US Patent 5,086,031 (see especially the Examples) and is incorporated herein by reference. Such a process of pelletisation or extrusion does not involve any steam treatment steps and the porosity of the support is derived from the interstices formed during the pelletisation or extrusion step of the non-porous silica. The silica support is suitably in the form of pellets or beads or are globular in shape having a particle diameter of 2 to 10 mm, preferably 4 to 6 mm. The siliceous support suitably has a pore volume in the range from 0.3-1.2 ml/g, preferably from 0.6-1.0 ml/g. The support suitably has a crush strength of at least 2 Kg force, suitably at least 5 Kg force, preferably at least 6 Kg and more preferably at least 7 Kg. The crush strengths quoted are based on average of that determined for each set of 50 beads/globules on a CHATTILLON tester which measures the minimum force necessary to crush a particle between parallel plates. The bulk density of the support is suitably at least 380 g/l, preferably at least 440 g/l.

The support suitably has an average pore radius (prior to use) of 10 to 500 Angstroms, preferably an average pore radius of 30 to 100 Angstroms.

In order to achieve optimum performance, the siliceous support is suitably free of extraneous metals or elements which might adversely affect the catalytic activity of the system. The siliceous support suitably has at least 99% w/w purity, ie the impurities are less than 1% w/w, preferably less than 0.60% w/w and more preferably less than 0.30% w/w.

Another pelleted silica support is the Grace silica No. 1371 which has an average bulk density of about 0.39 g/ml, an average pore volume of about 1.15 ml/g and an average particle size ranging from about 0.1-3.5 mm. These pellets can be used as such or after crushing to an average particle size in the range from 0.5-2 mm and sieving before being used as the support for the heteropolyacid catalyst.

The term "heteropolyacids" as used herein and throughout the specification is meant to include the free acids. The heteropolyacids used to prepare the olefin hydration catalysts of the present invention therefore include the free acids in which the anion is a complex, high molecular weight entity. Typically, the anion comprises 2-18 oxygen-linked polyvalent metal atoms, which are called peripheral atoms. These peripheral atoms surround one or more central atoms in a symmetrical manner. The peripheral atoms are usually one or more of molybdenum, tungsten, vanadium, niobium, tantalum and other metals. The central atoms are usually silicon or phosphorus but can comprise any one of a large variety of atoms from Groups I-VIII in

the Periodic Table of elements. These include, for instance, cupric ions; divalent beryllium, zinc, cobalt or nickel ions; trivalent boron, aluminium, gallium, iron, cerium, arsenic, antimony, phosphorus, bismuth, chromium or rhodium ions; tetravalent silicon, germanium, tin, titanium, zirconium, vanadium, sulphur, tellurium, manganese nickel, platinum, thorium, hafnium, cerium ions and other rare earth ions; pentavalent phosphorus, arsenic, vanadium, antimony ions; hexavalent tellurium ions; and heptavalent iodine ions. Such heteropolyacids are also known as "polyoxoanions", "polyoxometallates" or "metal oxide clusters". The structures of some of the well known anions are named after the original researchers in this field and are known eg as Keggin, Wells-Dawson and Anderson-Evans-Perloff structures.

Heteropolyacids usually have a high molecular weight eg in the range from 700-8500 and include dimeric complexes. They have a relatively high solubility in polar solvents such as water or other oxygenated solvents, especially if they are free acids and in the case of several salts, and their solubility can be controlled by choosing the appropriate counterions. Specific examples of heteropolyacids that may be used as the catalysts in the present invention include:

12-tungstophosphoric acid	-	$H_3[PW_{12}O_{40}] \cdot xH_2O$
12-molybdophosphoric acid	-	$H_3[PMo_{12}O_{40}] \cdot xH_2O$
12-tungstosilicic acid	-	$H_4[SiW_{12}O_{40}] \cdot xH_2O$
12-molybdosilicic acid	-	$H_4[SiMo_{12}O_{40}] \cdot xH_2O$
Potassium tungstophosphate	-	$K_6[P_2W_{18}O_{62}] \cdot xH_2O$
Sodium molybdophosphate	-	$Na_3[PMo_{12}O_{40}] \cdot xH_2O$
Ammonium molybdodiphosphate	-	$(NH_4)_6[P_2Mo_{18}O_{62}] \cdot xH_2O$
Sodium tungstonicelate	-	$Na_4[NiW_6O_{24}H_6] \cdot xH_2O$
Ammonium molybdodibaltate	-	$(NH_4)[Co_2Mo_{10}O_{36}] \cdot xH_2O$
Cesium hydrogen tungstosilicate	-	$Cs_3H[SiW_{12}O_{40}] \cdot xH_2O$
Potassium molybdodivanado phosphate	-	$K_5[PMoV_2O_{40}] \cdot xH_2O$

The impregnated support is suitably prepared by dissolving the heteropolyacid, which is preferably a tungstosilicic acid, in eg distilled water, and then adding the support to the aqueous solution so formed. The support is suitably left to soak in the acid solution for a duration of several hours, with periodic manual stirring, after which time it is suitably filtered using a Buchner funnel in order to remove any excess acid.

The wet catalyst thus formed is then suitably placed in an oven at elevated temperature for several hours to dry, after which time it is allowed to cool to ambient temperature in a desiccator. The weight of the catalyst on drying, the weight of the

support used and the weight of the acid on support was obtained by deducting the latter from the former from which the catalyst loading in g/litre was determined.

Alternatively, the support may be impregnated with the catalyst using the incipient wetness technique with simultaneous drying on a rotary evaporator.

This supported catalyst (measured by weight) can then be used in the esterification process. The amount of heteropolyacid deposited/impregnated on the support for use in the esterification reaction is suitably in the range from 10 to 60% by weight, preferably from 30 to 50% by weight.

In the esterification reaction, the olefin reactant used is suitably ethylene, propylene or mixtures thereof. Where a mixture of olefins is used, the resultant product will inevitably be a mixture of esters. The source of the olefin reactant used may be a refinery product or a chemical grade olefin which invariably contains some alkanes admixed therewith.

The saturated, lower aliphatic mono-carboxylic acid reactant is suitably a C1-C4 carboxylic acid and is preferably acetic acid.

The reaction mixture suitably comprises a molar excess of the olefin reactant with respect to the acetic acid reactant.

The reaction is carried out in the vapour phase suitably above the dew point of the reactor contents comprising the reactant acid, any alcohol formed *in situ*, the product ester and optionally some water. Dew point is the temperature at which condensation of a vapour of a given sample in air takes place. The dew point of any vaporous sample will depend upon its composition. The supported heteropolyacid catalyst is suitably used as a fixed bed which may be in the form of a packed column. The vapours of the reactant olefins and acids are passed over the catalyst suitably at an GHSV of 100 to 5000 per hour, preferably from 300 to 2000 per hour.

The esterification reaction is suitably carried out at a temperature in the range from 150-200°C using a reaction pressure which is at least 400KPa, preferably from 500-3000 Kpa depending upon the relative mole ratios of olefin to acid reactant and the amount of water used.

The reaction mixture may optionally contain steam if it is desired to generate a mixture of esters and alcohols in the process. The products of the reaction are recovered by eg fractional distillation. Where the esters are produced, whether singly or as mixture of esters, these may be hydrolysed to the corresponding alcohols or mixture of alcohols in relatively high yields and purity.

By using this latter technique the efficiency of the process to produce alcohols from olefins is significantly improved over the conventional process of producing alcohols by hydration of olefins.

The present invention is further illustrated with reference to the following Examples and Comparative Tests.

Example I:

Catalyst Preparations:

Catalyst 1. 12-Tungstophosphoric acid [$\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot 24\text{H}_2\text{O}$] (175 g) was dissolved in distilled water (250 ml). Lithium nitrate [$\text{LiNO}_3 \cdot 2\text{H}_2\text{O}$] (0.652 g) was dissolved in distilled water (~ 5ml). The lithium nitrate solution was added dropwise to the tungstophosphoric acid solution to form Solution "A".

Solution "A" was added to pelleted silica support (Grace 1371 grade, 1-3 mm, 99.5 g, ex W R Grace) and left to soak over 24 hours with occasional stirring in order to impregnate the silica with the tungstophosphoric acid catalyst. After this duration, excess solution "A" was decanted and filtered off. The resultant catalyst impregnated support was then dried in flowing nitrogen gas initially at 150°C for 3 hours and then raised to 200°C and maintained at that temperature for 5 hours. The supported catalyst so formed was then left in a desiccator to cool and was finally reweighed. The resultant supported catalyst had a final weight of 164.4 g, a net catalyst loading of 64.9 g and had the formula $\text{Li}_{0.1}\text{H}_{2.9}\text{PW}_{12}\text{O}_{40} \cdot 24\text{H}_2\text{O} / \text{SiO}_2$ corresponding to a loading of 255 g/l.

Catalyst 2. Pelleted silica support (Grace 1371 grade, 1-3 mm, 70 g, ex W R Grace) was soaked in a solution (250 ml) of 12-tungstosilicic acid [$\text{H}_4\text{SiW}_{12}\text{O}_{40} \cdot 26\text{H}_2\text{O}$] (65.53 g in distilled water) for 24 hours with intermittent stirring in order to impregnate the support with the catalyst. Thereafter the excess solution of the tungstosilicic acid was removed by decantation and filtration. The resultant catalyst impregnated support was then dried overnight under flowing nitrogen at 120°C. The dried supported catalyst so formed was cooled in a desiccator and had a final weight of 86.2g, a net catalyst loading of 16.2 g and had the formula $\text{H}_4\text{SiW}_{12}\text{O}_{40} \cdot 26\text{H}_2\text{O} / \text{SiO}_2$ corresponding to a loading of 92 g/l.

The above catalysts were used to esterify ethylene with acetic acid. The relative amounts of each of these catalysts used, their bed size and bed length in performing the esterification reaction were as follows:

Parameter	Catalyst 1	Catalyst 2
Volume (cm ³)	25	25
Weight (g)	15.5	11.2-11.4
Pellet size (mm)	1-2	1-2 (Table 2) & 0.5-1 (Tables 3, 4 and 5)
Bed length	8.5	8.75

The reaction conditions used and the results achieved are tabulated below.

5 In these tables, the following abbreviations have been used:

HOS

Hours on stream

Bed (T/M/B)

Bed (top/middle/bottom)

HAC

Acetic Acid

C₂H₄

Ethylene

10 H₂O/

Water

EtAc

Ethyl acetate

EtOH

Ethanol

DEE

Diethyl ether

GHSV

Gas hourly space velocity

15 g/Lcat/h

Gram per litre of catalyst per hour

STP

Standard temperature & pressure

STY

Space time yield

20

25

TABLE 1
(Catalyst 1 - 15.5 g)

Run Conditions:

Parameters	Run No. 1	Run No. 2	Run No. 3
HOS	1-3	19-21	25-27
Temperature (°C)			
Applied	170	170	170
Bed (T/M/B)	173.5/-/170.5	172/-/169	172/-/169
Pressure (Kpa)	1000	1000	1000
Total feed GHSV/h (@ STP)	979	979	979
C ₂ H ₄ GHSV/h	905	905	905
HAC GHSV/h	65	65	65
H ₂ O GHSV/h	9	9	9
C ₂ H ₄ (g/Lcat/h)	1131	1131	1131
HAC (g/Lcat/h)	173	173	173
H ₂ O (g/Lcat/h)	8	8	8
Feed contact time [1/GHSV](secs)	4	4	4
C ₂ H ₄ /HAC/ H ₂ O mole % ratio	92.4/6.6/1.0	92.4/6.6/1.0	92.4/6.6/1.0
C ₂ H ₄ /HAC/ H ₂ O wt % ratio	86.2/13.2/0.6	86.2/13.2/0.6	86.2/13.2/0.6
C ₂ H ₄ /HAC/ H ₂ O mole ratio	14.0	14.0	14.0

Product Analysis (Table 1 continued):

Products/Analysis	Run No. 1	Run No. 2	Run No. 3
HAC Conversion	51	47	45
Product Selectivity (wt %)			
EtAc	89.7	98.0	97.7
EtOH	0.5	0.5	0.4
DEE	0.9	0.7	1.0
Acetaldehyde	0.0	0.0	0.0
Oligomers	7.0	0.4	0.7
Others	1.90	0.49	0.26
EtAc Yield	45	46	44
EtAc STY (g/Lcat/h)	128	122	118
Carbon Balance (mol %)	102	102	105
Oxygen Balance (mol %)	86	89	100
Mass Balance	101	101	104
Water recovered (%)	90	70	81

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TABLE 2
(Catalyst 2 - 11.3 g)

Run Conditions:

Parameters	Run No. 1	Run No. 2	Run No. 3
HOS	1-2	17-20	21-24
Temperature (°C)			
Applied	170	170	170
Bed (T/M/B)	176/-/174	173/-/170	173/-/170
Pressure (Kpa)	1000	1000	1000
Total feed GHSV/h (@ STP)	980	980	980
C ₂ H ₄ GHSV/h	905	905	905
HAC GHSV/h	66	66	66
H ₂ O GHSV/h	9	9	9
C ₂ H ₄ (g/Lcat/h)	1131	1131	1131
HAC (g/Lcat/h)	177	177	177
H ₂ O (g/Lcat/h)	8	8	8
Feed contact time [1/GHSV](secs)	4	4	4
C ₂ H ₄ /HAC/ H ₂ O mole % ratio	92.3/6.7/1.0	92.3/6.7/1.0	92.4/6.6/1.0
C ₂ H ₄ /HAC/ H ₂ O wt % ratio	85.9/13.5/0.6	85.9/13.5/0.6	86.2/13.2/0.6
C ₂ H ₄ /HAC/ H ₂ O mole ratio	13.7	13.7	13.7

Product Analysis (Table 2 continued):

Products/Analysis	Run No. 1	Run No. 2	Run No. 3
HAC Conversion	62	66	64
Product Selectivity (wt %)			
EtAc	86.0	97.3	97.6
EtOH	2.4	0.4	0.4
DEE	3.3	1.8	1.4
Acetaldehyde	0.0	0.0	0.0
Oligomers	2.4	0.3	0.6
Others	5.9	0.1	0.1
EtAc Yield	53	65	62
EtAc STY (g/Lcat/h)	151	180	171
Carbon Balance (mol %)	101	104	105
Oxygen Balance (mol %)	98	95	99
Mass Balance	101	103	105
Water recovered (%)	70	69	67

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TABLE 3
(Catalyst 2 - 11.2 g)

Run Conditions:

Parameters	Run No. 1	Run No. 2	Run No. 3
HOS	19.25-22.5	23-26	43.25-46.25
Temperature (°C)			
Applied	170	170	180
Bed (T/M/B)	172.5/176/-	172.5/175.5/-	182/187/-
Pressure (Kpa)	1000	1000	1000
Total feed GHSV/h (@ STP)	980	980	980
C ₂ H ₄ GHSV/h	905	905	905
HAC GHSV/h	66	66	66
H ₂ O GHSV/h	9	9	9
C ₂ H ₄ (g/Lcat/h)	1131	1131	1131
HAC (g/Lcat/h)	177	177	177
H ₂ O (g/Lcat/h)	8	8	8
Feed contact time [1/GHSV](secs)	4	4	4
C ₂ H ₄ /HAC/ H ₂ O mole % ratio	92.3/6.7/1.0	92.3/6.7/1.0	92.3/6.7/1.0
C ₂ H ₄ /HAC/ H ₂ O wt % ratio	86/13.4/0.6	86/13.4/0.6	86/13.4/0.6
C ₂ H ₄ /HAC/ H ₂ O mole ratio	13.7	13.7	13.7

Product Analysis (Table 3 continued):

Products/Analysis	Run No. 1	Run No. 2	Run No. 3
HAC Conversion	72	72	82
Product Selectivity (wt %)			
EtAc	96.0	94.4	94.9
EtOH	0.5	0.5	0.7
DEE	2.9	2.7	3.3
Acetaldehyde	0.0	0.0	0.0
Oligomers	0.4	1.6	0.7
Others	0.2	0.7	0.3
EtAc Yield	69	68	78
EtAc STY (g/Lcat/h)	203	194	210
Carbon Balance (mol %)	101	103	108
Oxygen Balance (mol %)	91	97	104
Mass Balance	100	103	108
Water recovered (%)	47	48	48

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TABLE 4
(Catalyst 2 - 11.2 g)

Run Conditions:

Parameters	Run No. 1	Run No. 2	Run No. 3
HOS	47-50	67.25-70.25	71-74
Temperature (°C)			
Applied	180	190	190
Bed (T/M/B)	181.5/186.5/-	191.5/196/-	191.5/195.5/-
Pressure (Kpa)	1000	1000	1000
Total feed GHSV/h (@ STP)	980	980	980
C ₂ H ₄ GHSV/h	905	905	905
HAC GHSV/h	66	66	66
H ₂ O GHSV/h	9	9	9
C ₂ H ₄ (g/Lcat/h)	1131	1131	1131
HAC (g/Lcat/h)	177	177	177
H ₂ O (g/Lcat/h)	8	8	8
Feed contact time [1/GHSV](secs)	4	4	4
C ₂ H ₄ /HAC/ H ₂ O mole % ratio	92.3/6.7/1.0	92.3/6.7/1.0	92.3/6.7/1.0
C ₂ H ₄ /HAC/ H ₂ O wt % ratio	86/13.4/0.6	86/13.4/0.6	86/13.4/0.6
C ₂ H ₄ /HAC/ H ₂ O mole ratio	13.7	13.7	13.7

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Product Analysis (Table 4 continued):

Products/Analysis	Run No. 1	Run No. 2	Run No. 3
HAC Conversion	79	74	72
Product Selectivity (wt %)			
EtAc	95.2	94.7	94.9
EtOH	0.7	0.7	0.7
DEE	3.2	2.8	2.2
Acetaldehyde	0.0	0.0	0.0
Oligomers	0.6	1.4	1.3
Others	0.2	0.3	0.8
EtAc Yield	75	70	68
EtAc STY (g/Lcat/h)	206	202	191
Carbon Balance (mol %)	105	102	104
Oxygen Balance (mol %)	102	94	99
Mass Balance	105	102	104
Water recovered (%)	47	52	54

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TABLE 5
(Catalyst 2 - 11.4 g)

Run Conditions:

Parameters	Run No. 1	Run No. 2	Run No. 3
HOS	19-22	44-47	68.75-71.75
Temperature (°C)			
Applied	180	180	180
Bed (T/M/B)	181.5/186/182.5	181.5/185/182	181.3/184.5/181.2
Pressure (Kpa)	1000	1000	1000
Total feed GHSV/h (@ STP)	980	980	980
C ₂ H ₄ GHSV/h	905	905	905
HAC GHSV/h	66	66	66
H ₂ O GHSV/h	9	9	9
C ₂ H ₄ (g/Lcat/h)	1131	1131	1131
HAC (g/Lcat/h)	177	177	177
H ₂ O (g/Lcat/h)	8	8	8
Feed contact time [1/GHSV](secs)	4	4	4
C ₂ H ₄ /HAC/ H ₂ O mole % ratio	92.3/6.7/1.0	92.3/6.7/1.0	92.3/6.7/1.0
C ₂ H ₄ /HAC/ H ₂ O wt % ratio	86/13.4/0.6	86/13.4/0.6	86/13.4/0.6
C ₂ H ₄ /HAC/ H ₂ O mole ratio	13.7	13.7	13.7

Product Analysis (Table 5 continued):

Products/Analysis	Run No. 1	Run No. 2	Run No. 3
HAC Conversion	71	64	60
Product Selectivity (wt %)			
EtAc	95.9	97.2	97.8
EtOH	0.7	0.6	0.5
DEE	2.3	1.8	1.3
Acetaldehyde	0.0	0.0	0.0
Oligomers	0.8	0.3	0.3
Others	0.3	0.1	0.0
EtAc Yield	68	63	59
EtAc STY (g/Lcat/h)	194	183	164
Carbon Balance (mol %)	100	100	100
Oxygen Balance (mol %)	94	89	93
Mass Balance	100	99	99
Water recovered (%)	53	56	62

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